DEUTERIUM SPECIATION IN CHONDRITIC ORGANIC SOLIDS: A RELIC OF COLD MOLECULAR PROCESSES.

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Introduction: One of the hallmark properties of primitive organic solids (IOM) in type 1 & 2 chondrites is the high deuterium content relative to Galactic and Solar values [1]. The high D enrichment in IOM has largely been attributed to small molecule chemistry that occurred, prior to the synthesis of IOM, in the InterStellar Medium (ISM) at very low temperatures where extensive fractionation can occur through ion-molecule reactions (predominantly reactions with H_2D^+ and CH_2D^+). The potential for heavy D enrichment is revealed through the detection of highly deuterated formaldehyde and methanol with D/H ratios up to 10^{-2} [2]. Extremely D enriched formaldehyde and methanol (up to D_2CO and CD_3OH) have also been observed in the early "hot corino" stage of molecular cloud collapse and early Solar System formation [3]. Placing these very high D enrichments in context, it is noteworthy that even highly D enriched chondritic IOM, e.g. the CR1 chondrite GRO95577 [4] with a bulk δD of 3235 ‰, is only slightly enriched relative to terrestrial water (by a factor of ∼ 4 x). Thus, while isotopically IOM is exotic relative to terrestrial D/H, it is by no means close to the enrichments observed for small molecules in the ISM and cold molecular clouds.

This fact has been recognized by others [5], who proposed that previously formed IOM (by an unstated mechanism) initially has a very low D/H but was enriched in D in the outer regions of the Solar System at temperatures on the order of 120 K, via D-H exchange of IOM with H_2D^+. It was further proposed that different bonds will exchange D with H at rates proportional to their bond strength, thus benzylic carbon was predicted to be isotopically heavier then aliphatic carbon that is predicted to be isotopically heavier than aromatic H. In the case of IOM derived from Orgueil (CI1) it was concluded that for benzylic carbon δD = 1250‰, aliphatic carbon δD =550‰, and aromatic carbon δD =150‰.

Direct detection of deuterium substitution via solid-state ^2H NMR provides an unambiguous means of assessing whether there exists any detectible difference in D abundance amongst organic functional groups. The problem is that natural abundance ^2H NMR is one of the least sensitive NMR experiments, e.g. for terrestrial values of D, the sensitivity of ^2H NMR is 1.45×10^{-6} that of ^1H NMR. Furthermore, ^2H NMR spectra are complicated by the fact that deuterium is a spin 1 quadrupole, which means that the spectrum appears as a series of rotational echos spread out over the frequency range of the quadrupole interaction, up to 140 Khz for D in rigid environments. Notwithstanding this difficulty we have developed an experimental protocol that allows us to obtain purely isotropic ^2H NMR spectra, devoid of the quadrupolar artifacts. We can then compare these spectra with ^1H NMR spectra to assess the local variation in D enrichment. It should be noted that the frequency distribution of D-functional groups in ^2H NMR spectra are nearly identical with the distribution of H-functional groups in ^1H NMR spectra, with the exception of a small frequency shift associated with the scalar quadrupolar shift.
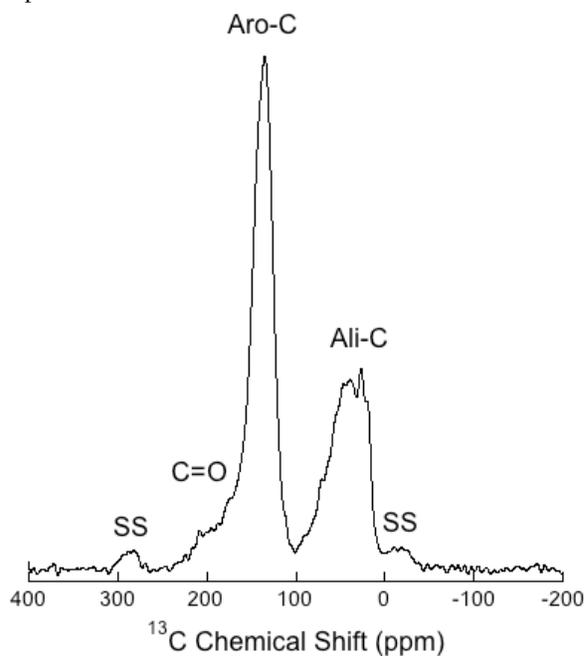
Figure 1: ^{13}C solid state NMR spectrum of IOM isolated from the CR1 chondrite GRO95577, revealing that ∼ 54 % of the carbon is aromatic, 36 % of the carbon is aliphatic, and the remainder is in the form of carbonyl bearing functional groups. SS = spinning side bands.

The ^{13}C solid state NMR spectrum (fig. 1) of IOM isolated from the CR1 chondrite GRO95577 reveals a complex, highly aliphatic and aromatic, macromolecule with an aromatic carbon content similar to that of the CR2 EET92042 [6]. The broad spectral range of saturated carbon (∼ 10 up 90 ppm) is indicative of a wide range of sp^3 carbon environments, a significant fraction of these being bonded to oxygen.

In fig. 2 the ^1H NMR spectrum of GRO 95577 IOM is presented revealing a predominance of aliphatic H over aromatic H (∼ 60:40). The broad lines reflect considerable dipolar broadening. The relatively low frequency of the aliphatic H peak (at 1.2 ppm), is consistent with H in predominantly alicyclic structures. Benzylic H (2.35-3.9) and R-OH (4-5 ppm) are not strongly represented, but could be present at the 2 to 5 % level. Based on this H distribution and if deuteration occurs through reactions of H_2D^+ with initially depleted IOM (e.g., -840 ‰), as proposed in [5], then we expect the the ^2H NMR spectrum to exhibit slightly more intense ali-D over aro-D based on $\alpha_{ali-aro}$= $(D/H_{ali}/D/H_{aro})$ = 1.45; i.e., increased predominance of ali-D over aro-D (∼ 70:30).
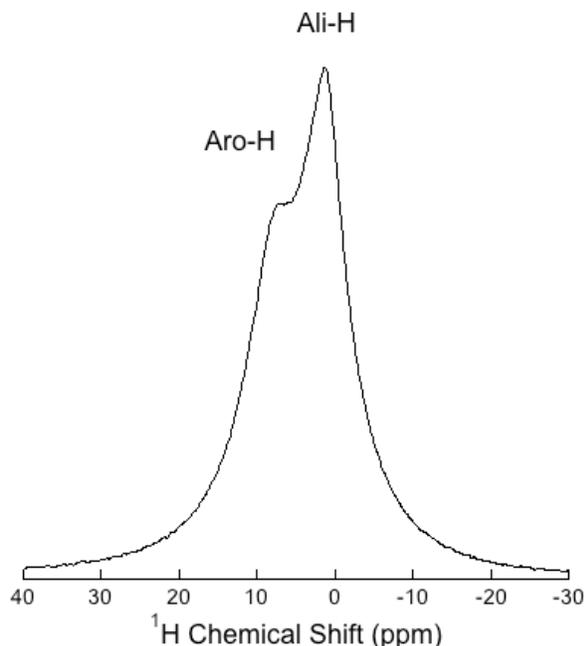
Figure 2: ^{1}H MAS NMR spectrum of IOM isolated from the CR1 chondrite GRO95577. Clearly revealed are peaks associated with aromatic H (at 8.0 ppm) and aliphatic H (at 1.2 ppm, consistent with predominantly alicyclic H, distal from unsaturated carbon). Note that benyzl H is expected at 2.35-3.9 ppm and is, therefore, a minor H-constituent.

The corresponding ^{2}H NMR spectrum is presented in Fig. 3 and reveals a very strong predominance of aliphatic (not benzylic) deuterons over aromatic deuterons. Note that the Ali-D frequency is very low ($\sim$ 0.5 ppm); likely suggesting the ali-D carrier is predominantly CH_3 bonded to ali-cyclic moieties. Aliphatic carbon bonded to unsaturated carbon, e.g. benzylic CH_3 groups, are expected at higher frequencies ($\sim$ 2.5 ppm). Aromatic D at 7.8 ppm is virtually non-observable (we fit a band to accommodate a potential maximum aromatic D of 5 %, Fig. 3). The obvious asymmetry of the ^{2}H NMR spectrum requires that we fit an additional peak at 3.7 ppm that reasonably assigned to R-OD groups (Fig. 3).

Given the elemental H/C ratio, bulk δD, the ^{1}H and ^{2}H NMR data we can determine the D/H content of the specific sites. For example, we find that the aliphatic carbon has δD of 4650 ‰ whereas the aromatic carbon is relatively depleted at – 500 ‰. Indicating that $\alpha_{ali-aro} = (D/H_{ali}/D/H_{aro}) = 11.4$, a factor nearly 8 times larger than predicted in [5].

Such a distribution is not consistent with exchange with H_2D^+ at 120 K, rather it is more likely a relic of a much higher initial bulk δD in IOM that has been "eroded" to lower D enrichment by D/H exchange with D depleted H_2O during parent body processing where D/H exchange amongst aliphatic D is much slower than that of aromatic D.
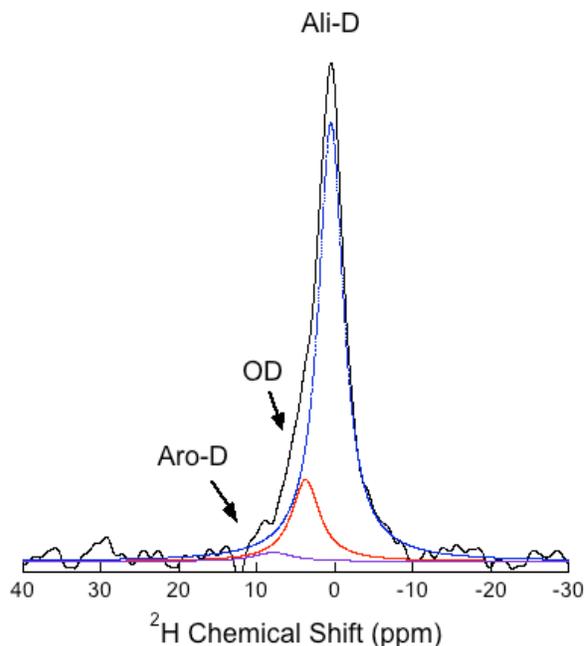
Figure 3: Solid state ^{2}H NMR of IOM isolated from the CR1 chondrite GRO95577. The Ali-D appears at 0.5 ppm, a shoulder at 3.7 ppm is consistent with OD, a maximum of $\sim$ 4 % aro-D (at 7.8 ppm) can be fit to the data.

In order to test this we heated a bituminous coal in 5 % D_2O at 120 °C for seven days. Considerable D-H exchange occurred, both on the aromatic and aliphatic carbon. Interestingly, whereas the aliphatic region of the ^{1}H NMR spectrum peaks at 0.6 ppm (polymethylene-H), in the ^{2}H NMR spectrum, the ali-D peaks at 1.6 ppm consistent with aliphatic C proximal to unsaturated carbon (e.g., benzylic carbon). In this case the D-H exchange occurs through an ionic mechanism (e.g. carbocation) and is unrelated to the C-H bond strengths.

The most conservative intepretation of D/H speciation in IOM, therefore, is that originally IOM was highly enriched, having been derived from a D-enriched precursor. Subsequent D-H exchange by a much less D rich parent body fluid, yields much less D-enriched IOM, and where the remnant D resides on the functional groups that exchange the slowest.

References: [1] Robert F. and Epstein S. (1982) *GCA, 46,* 81-95. [2] Millar T. J. et al. (1989) *APJ., 340,* 906-920. [3] Loinard L. et al. (2002) *Planet Space Sci.,* 50, 1205-1213. [4] Alexander C. M. O'D. et al. (2007) *GCA, 71*, 4380-4403. [5] Remusat L. et al. (2006) *EPSL, 243,* 15-25.[6] Cody G. D. and Alexander C. M. O'D. (2005) *GCA, 69,* 1085-1097.